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CLEAN-BURNING CARBONACEOUS COMPOSITIONS

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This invention relates to carbonaceous materials which are to be burned, and more particularly to compositions containing a liquid carbonaceous material having dispersed therein an organic salt of a transition element of atomic number in the range of 21 to 30, inclusive, which compositions are relatively stable at ordinary temperatures and are relatively clean-burning under combustion conditions.

In one aspect, the invention relates to lubricating oils or lubricants which are subjected to combustion conditions, as in an internal combustion engine in which some of the lubricating oil passes into the combustion chamber. Such oils are generally composed primarily of hydrocarbons. It is desirable that the carbonaceous materials in the combustion chamber burn cleanly, that is, leave no carbon deposit.

In another aspect, the invention relates to various liquid carbonaceous fuels such as gasoline, and the like low boiling materials; and Diesel fuels, jet fuels, fuel oils and the like high boiling materials. These fuels are primarily hydrocarbons. It is desirable that these materials burn cleanly under combustion conditions, that is, leave no carbon or soot deposit in the combustion chamber or in the exhaust or flue lines.

For convenience, the term "liquid hydrocarbon oil" is used to indicate any liquid hydrocarbon, including liquefied hydrocarbons such as methane and the like alkanes under pressure, gasoline, Diesel fuel, fuel oil, gas oil, kerosene, lubricating oils, etc. The liquid hydrocarbon oil may contain small amounts of other substances such as additives, silicones, and the like.

It has been proposed heretofore to add an organic salt of a metal to lubricating oils in order to provide an oil which tends to avoid the formation of carbon deposits in the combustion zone of an internal combustion engine.

In accordance with the invention, it has been found that combinations of two transition elements in a dispersible form such as salts, soaps, esters, alcoholates, and the like, said element having an atomic number of 21 to 30, are much more effective as combustion catalysts for carbonaceous materials than are the single metal compounds.

The objects achieved in accordance with the invention include the provision of combustible carbonaceous materials (especially liquid hydrocarbon oils) which are relatively clean-burning; the provision of a method of improving the burning qualities of combustible carbonaceous materials; the provision of carbonaceous lubricants which tend to promote the clean-burning of carbonaceous materials in the combustion zone and

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at the same time have a high crankcase stability; and other objects which will be apparent as details and embodiments of the invention are set forth hereinafter.

The materials employed comprise the metals having an atomic number of 21 to 30, i. e., of scandium, titanium,vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc, which may be in the form of salts of carboxylic acids, such as abietates, stearates, oleates and naphthenates, organic sulfonates, organic sulfates, organic phosphates, organic phosphonates and organic thiophosphates. The metal may be in the negative radical such as vanadates, chromates, manganates, etc., or it may be in the form of an alcoholate or the like. These elements are known as transition elements. They have the common property, as to the arrangement of electrons, that the ten $3d$ orbits are occupied in preference to the incomplete N shell. Chromium and copper have the additional property of being represented as if a $4s$ electron has reverted to the $3d$ orbit.

The amount of the combination of the metal compounds to be used with the carbonaceous material will depend upon the intended use, as well as the characteristics of the carbonaceous material. In general from 0.1% to about 3% is suitable. Even small amounts show a significant improvement. There is no upper limit, since the organic compounds in themselves are combustible materials; however, it would be uneconomical to add more than is necessary to impart the desired properties. The compounds should be thoroughly dispersed in the carbonaceous material for best results, and should be compounds which are dispersible. Some combustible materials are relatively clean-burning and would require relatively small amounts of the salt combinations. On the other hand, other carbonaceous materials which are not clean-burning would require larger amounts of the salt combinations.

The following examples illustrate the scope of the invention:

A

A medium viscosity crankcase lubricating oil containing about 1% (all parts or per cent are by weight unless otherwise indicated herein) of any one of the following combinations:

1. 1 to 3 parts Chromium stearate
   1 to 3 parts Vanadium oleate
2. 1 to 3 parts Titanium abietate
   1 to 3 parts Chromium naphthenate

3.	1 to 3 parts	Manganese lauryl sulfate
	1 to 3 parts	Iron abietate
4.	1 to 3 parts	Nickel monooctyl phosphate
	1 to 3 parts	Copper stearate
5.	1 to 3 parts	Copper monophenyl phosphate
	1 to 3 parts	Zinc lauryl sulfonate
6.	1 to 3 parts	Chromium 2-ethyl hexoate
	1 to 3 parts	Manganese diamyl benzoate
	1 to 3 parts	Iron abietate
7.	1 to 3 parts	Chromium palmitate
	1 to 3 parts	Titanium monomyristyl sulfate
	1 to 3 parts	Managanese dicresyl phosphate
8.	1 to 3 parts	Zinc tetrabutyl phthalate
	1 to 3 parts	Copper naphthenate
	1 to 3 parts	Nickel monolauryl thiophosphate
9.	1 to 3 parts	Cobalt stearate
	1 to 3 parts	Iron dibutyl phthalate
	1 to 3 parts	Manganese monocresyl phosphate
10.	1 to 3 parts	Chromium hexadecyl sulfonate
	1 to 3 parts	Vanadyl tri monocetyl phosphate
	1 to 3 parts	Titanium abietate

B

Gasoline containing about 1% of any one of the following combinations:

11.	1 to 3 parts	Zinc stearate
	1 to 3 parts	Copper myristate
12.	1 to 3 parts	Nickel abietate
	1 to 3 parts	Cobalt caprylate
13.	1 to 3 parts	Iron caproate
	1 to 3 parts	Manganese caprate
14.	1 to 3 parts	Chromium naphthenate
	1 to 3 parts	Hexadecyl vanadate
15.	1 to 3 parts	Titanium laurate
	1 to 3 parts	Manganese lauryl sulfonate
16.	1 to 3 parts	Vanadium stearate
	1 to 3 parts	Chromium monooctyl sulfate
	1 to 3 parts	Manganese diamyl phosphate
17.	1 to 3 parts	Stearyl vanadate
	1 to 3 parts	Titanium stearate
	1 to 3 parts	Zinc laurate
18.	1 to 3 parts	Manganese abietate
	1 to 3 parts	Iron monolauryl thiophosphate
	1 to 3 parts	Cobalt linoleate
19.	1 to 3 parts	Zinc palmitate
	1 to 3 parts	Copper lauryl sulfonate
	1 to 3 parts	Nickel abietate
20.	1 to 3 parts	Iron dihexyl phosphate
	1 to 3 parts	Nickel monooctyl phosphonate
	1 to 3 parts	Chromium stearate

The following tests of carbonaceous materials containing combinations of organic salts, in accordance with the invention, will serve to illustrate and point out some of the advantages but in no wise to limit the scope of the invention as described herein.

The burning characteristics of the carbonaceous material may be tested as follows: A 2.5 gram sample of the material is placed in a 70 mm. diameter glass Petri dish, and then the latter is placed in an electrically heated furnace for 16 hours at 525° F. followed by 4 hours at 750° F. The weight of the carbon residue is then determined, and may be expressed conveniently as per cent by weight of the original sample. A perfectly clean-burning material leaves a zero per cent residue, whereas, a material which has poor burning characteristics leaves a high residue.

The following data is typical (per cent is by weight, based on the oil):

	Per cent residue
Oil alone: Solvent extracted oil, avg.	13.3
Oil with single salts:	
Oil plus saturated chromium oleate (less than 0.5%)	16.2
Oil plus 0.5% chromium naphthenate	11.1
Oil plus 0.5% copper oleate	5.1
Oil plus 0.5% manganese naphthenate	9.9
Oil plus 1.0% manganese naphthenate	11.1
Oil with two or more salts:	
Oil plus 0.5% chromium naphthenate plus 0.5% manganese naphthenate	0.6
Oil plus 0.25% chromium naphthenate plus 0.25% manganese naphthenate	0.5
Oil plus 0.25% manganese naphthenate plus 0.25% cobalt naphthenate	4.4
Oil plus 0.5% chromium naphthenate plus 0.5% copper oleate	0.7
Oil plus 0.25% iron naphthenate plus 0.25% chromium naphthenate	0.4
Oil plus 0.25% cobalt naphthenate plus 0.25% chromium naphthenate	2.3

It is apparent from the above data that combinations of at least two of the organic salts give a much lower residue than do combinations of the oil with the single salt, even though the total amount of salts present is not increased. This will be seen, for example, by comparing the residue from the oil plus 0.5 chromium naphthenate, and the residue from the oil plus 0.5% manganese naphthenate, with the residue from the oil plus 0.25% chromium naphthenate and 0.25% manganese naphthenate where an approximately 20-fold improvement is indicated.

As the art will appreciate in view of the above tests, the other combinations within the above general disclosure will also give comparably satisfactory results, in accordance with the broad aspects of the invention.

In a lubricating oil it is important that the added salts do not catalyze oxidation in the crankcase where such oxidation would prove harmful. In order to test this characteristic of the lubricating oil containing the salt combinations, samples were tested as above, except that the final four hour temperature was 650° F. rather than 750° F. The following results are typical:

	Per cent residue
Oil plus 0.5% chromium naphthenate plus 0.5% manganese naphthenate	26.5
Oil plus 0.5% chromium naphthenate plus 0.5% copper oleate	33.6
Oil plus 0.25% chromium naphthenate plus 0.25% cobalt naphthenate	28.3

The high residue obtained in these tests indicates that there is very little oxidation of the oil below burning temperatures even when as high as 650° F., and that the added salt combination would not catalyze oxidation in the crankcase.

If desired, the lubricating oils to which the salt combinations are added may also contain anti-oxidants such as organic compounds containing sulfur or phosphorus, or both, in elemental form or combined in an organic material. Typical anti-oxidants are tricresyl phosphate and phosphite, the reaction product of hydrogenated sperm oil or an olefin, mercaptan or alcohol with

phosphorus pentasulfide and metal, ester or amine derivatives thereof, thianthrene, quinone, hydroquinone, lecithin, para-amino phenol and alkyl derivatives thereof, an organic aliphatic amine such as cetyl dimethyl amine and a "methane base" such as tetramethyl diamino diphenyl methane. A small amount of any one or more thereof may be included in the above oil examples.

The following tests (carried out with a 650° F. final four hour temperature, as above) illustrate such combinations:

	Per cent residue
Oil plus 0.5% manganese naphthenate plus 0.5% chromium naphthenate plus 1.9% triphenyl phosphite	2.2
Oil plus 0.5% manganese naphthenate plus 0.5% chromium naphthenate plus 2.7% o-tricresyl phosphate	2.0
Oil plus 0.5% manganese naphthenate plus 0.5% chromium naphthenate plus 1.7% thianthrene	0.7
Oil plus 0.5% chromium naphthenate plus 0.5% manganese naphthenate plus 3.8% of reaction product of hydrogenated sperm oil and P_2S_5	2.9
Oil plus 0.5% manganese naphthenate plus 0.5% chromium naphthenate plus 0.5% sulfur	0.2
Oil plus 0.5% manganese naphthenate plus 0.5% chromium naphthenate plus 0.23% red phosphorus	5.2

It is evident from the foregoing data that the presence of the anti-oxidant does not appreciably alter the catalytic effect of the salt combination. In fact, the elemental sulfur combination shows improved effects.

The "Sohio" corrosion test was used in evaluating the effect of the added salts on the corrosion characteristics of a lubricating oil alone, and also on a lubricating oil containing the added salts plus the anti-oxidant obtained by reacting hydrogenated sperm oil with phosphorus pentasulfide. This test is described in a copending application of E. C. Hughes, J. D. Bartleson, M. L. Sunday and M. M. Fink (Serial No. 718,890, filed December 27, 1946).

Essentially the laboratory test equipment consists of a vertical thermostatically heated glass test tube (45 mm. outside diameter and 42 cm. long), into which is placed the corrosion test unit. An air inlet is provided for admitting air into the lower end of the corrosion unit in such a way that in rising the air will cause the oil and suspended material therein to circulate into the corrosion unit. The tube is filled with an amount of the oil to be tested which is at least sufficient to submerge the metals being tested.

The corrosion test unit essentially consists of a circular relatively fine grained copper-lead test piece of $\frac{13}{16}$'' O. D., which has a ¼'' diameter hole in its center (i. e., shaped like an ordinary washer). The test piece has an exposed copper-lead surface of 3.00 sq. cm. Of this surface area, 1.85 sq. cm. acts as a loaded bearing, and is contacted by a part of the cylindrical surface of a hardened steel drill rod (¼'' diameter and $\frac{21}{32}$'' long, and of 51–57 Rockwell hardness).

The drill rod is held in a special holder, and the holder is rotated so that the surface of the drill rod which contacts the bearing sweeps the bearing surface (the drill rod is not rotated on its own axis and the surface of the drill rod which contacts the bearing is not changed).

The corrosion test unit means for holding the bearing and the drill rod is a steel tubing (15'' long and $1\frac{1}{32}$'' O. D.) which is attached to a support. A steel cup (1'' long, $1\frac{1}{32}$'' O. D. by $\frac{13}{16}$'' I. D.) is threaded into the steel tube, at the lower end. The cup has a ⅜'' diameter hole in the bottom for admitting the oil into the corrosion chamber. The copper-lead test piece fits snugly into the steel cup and the hole in the test piece fits over the hole in the steel cup. A section of steel rod (⅜'' in diameter and 19'' long) serves as a shaft and is positioned by 2 bearings which are fixedly set in the outer steel tubing, one near the top and one near the lower (threaded) end thereof. Several holes are drilled just above and just below the lower bearing. The holes above the bearing facilitate cleaning the apparatus, while the holes below the bearing enable the circulation of oil through the corrosion chamber. The drill rod holder is connected to the shaft by a self-aligning yoke and pin coupling. This assures instantaneous and continuous alignment of the drill rod bearing member against the bearing surface at all times. A pulley is fitted to the top of the steel shaft and the shaft is connected therethrough to a power source. The shaft is rotated at about 675 R. P. M.; and the weight of the shaft and attached members is about 600 grams, which is the gravitational force which represents the thrust on the bearing. The air lift from the air inlet pumps the oil through the chamber containing the test piece and out throught the holes in the steel tubing.

The ratios of surface active metals to the volume of oil in an internal combustion test engine are nearly quantitatively duplicated in the test equipment. The temperature used is approximately that of the bearing surface. The rate of air flow per volume of oil is adjusted to the same as the average for a test engine in operation. Of the catalytic effects, those due to soluble iron are the most important. They are empirically duplicated by the addition of a soluble iron salt. Those due to lead-bromide are duplicated by its addition.

The test was correlated with a slightly modified version of the L–4 Chevrolet test. This modification comprised reducing the oil additions from the 4 quarts in the usual procedure to 2 quarts, by reducing the usual 1 pint oil additions which are made at 4 hour intervals to ½ pint additions. This modification increases the severity of the test in its corrosion and detergency components, particularly in the case of border line oils.

For each test, the glass parts are cleaned by the usual chromic acid method, rinsed and dried. The metal parts are washed with chloroform and carbon disulfide and polished with No. 925 emery cloth or steel wool. A new copper-lead test piece is used for every test. The test piece is polished before use, on a surface grinder to give it a smooth finish. The test piece is weighed before and after the test on an analytical balance to evaluate the corrosion. After placing the oil and corrosion test unit in the tube, and bringing the assembly up to temperature in the thermostat, soluble catalyst is added and the air flow is started. Lead bromide catalyst is added immediately after starting the air, and timing of the test is begun.

The laboratory test conditions which were found to correlate with the modified Chevrolet procedure 36-hour test are shown in the following table.

Table A

Temperature—325° F.
Oil sample—107 cc.
Air flow rate—70 liters/hour
Time—10 hours
Catalysts—Steel; copper-lead bearing: 3 sq. cm. area of which 1.85 sq. cm. is a bearing surface; ferric 2-ethyl hexoate: 0.05% as Fe_2O_3 in C. P. benzene; lead bromide: 0.1% as precipitated powder.
Bearing assembly:
Load ---------- grams -- 600
Speed ---------- R. P. M -- 675

By extending the laboratory test to 20 hours, it was found that correlation with the modified Chevrolet 72 hour test could be obtained.

At the close of the test period, the extent of corrosion is determined by reweighing the corrosion test piece and determining the change in weight due to the test. An accurate evaluation of the lacquering properties of an oil is obtained by a visual rating system which is applied to the outer surface of the corrosion unit steel tube and metal cup in much the same way that the piston skirt, cylinder wall, etc. of an engine are rated for varnishes. The sludge rating of the engine is simulated by a visual rating of the insoluble materials and used oil which are coated on the glass test tube at the conclusion of the test. For both sludge and varnish rating a scale rating of A (best) to F (worst) is used.

A sufficient volume of used oil is obtained from the test for determination of the usual used oil properties, such as pentane insolubles, viscosity increase, and neutralization number.

To show that the added salt combinations do not act as harmful pro-oxidants in the lubricating oil, e. g., under crankcase temperature conditions, tests (20 hour) were run on the oil alone, the oil plus the anti-oxidant, the oil plus a metal salt combination, and several compositions of oil plus the anti-oxidant plus the salt combinations.

The additive, reaction product of phosphorus pentasulfide with hydrogenated sperm oil, was prepared as follows:

Hydrogenated sperm oil is available under the trade name of "Spermofol No. 52." It has an iodine value of 6–7, a melting point of 50–52° C., a free fatty acid content (as oleic) of 1.0–2.0%, a saponification value of 135–138, and about 38% of unsaponifiables.

This hydrogenated sperm oil is reacted with 25% by weight of phosphorus pentasulfide at a temperature of about 300° F. After the reaction is complete, which under reaction conditions, takes four hours, the material is permitted to stand, after which the by-product residue settles and the reaction product is decanted; following this, it is filtered with the use of a filter aid. This additive is referred to as P_2S_5-Spermofol.

The following compositions were tested:

A—Oil alone (solvent extracted)
B—Oil plus 1% P_2S_5-Spermofol
C—Oil plus 0.25% chromium naphthenate plus 0.25% manganese naphthenate
D—Oil plus 1% P_2S_5-Spermofol plus 0.25% manganese naphthenate plus 0.25% chromium naphthenate
E—Oil plus 1% P_2S_5-Spermofol plus 0.50% manganese naphthenate plus 0.50% chromium naphthenate
F—Oil plus 1% P_2S_5-Spermofol plus 0.25% copper oleate plus 0.25% chromium naphthenate

The following results are typical:

Composition Tested	A	B	C	D	E	F
Sludge (isopentane insoluble, in milligrams)	0.26	0.42	0.49	0.05	0.03	0.44
Corrosion (in milligrams weight loss) of: Cu-Pb	40.1	55.2	55.0	53.0	40.4	22.8
Acid No	11.3	7.1	5.1	7.1	2.9	6.8
Viscosity Increase (SUS)	4,070	1,840	2,115	1,500	1,447	874
Lacquer Rating	A	A−	A	A	A−	A−
Sludge Rating	A−	A+	A−	A+	A+	A+

It is evident from the foregoing data that the presence of the salt combinations does not detract from the anti-oxidant characteristics imparted by anti-oxidant additive. In fact, the salt combination is actually beneficial and improves or supplements the effect of the anti-oxidant additives. Compare, for instance, tests of B and D as to sludge, viscosity increase, and corrosion characteristics, or tests B and E as to acid number, sludge, viscosity increase, and corrosion characteristics, or tests B and F as to acid number, viscosity increase, and corrosion characteristics. The marked reduction in corrosion in the latter is particularly noteworthy.

The specific examples given herein are illustrative, and not limitative. All embodiments of the invention give comparable results, as the art will understand in view of the disclosures herein.

In view of the foregoing disclosure, variations and modifications of the invention will be apparent to those skilled in the art, and the invention contemplates all such variations and modifications except as do not come within the scope of the appended claims.

We claim:

1. A lubricating composition which is relatively clean-burning and also relatively stable against oxidative deterioration at temperatures in the range of room temperature to crankcase temperatures, comprising a mineral lubricating oil as the essential and primary component having dispersed therein an amount within the range of 0.25 to 0.50% by weight of chromium naphthenate and an amount within the range of 0.25 to 0.50% by weight of a carboxylate salt selected from the group consisting of manganese naphthenate and copper oleate, to promote clean-burning at combustion temperatures, and as an anti-oxidant about 1% by weight of the reaction product of P_2S_5 with hydrogenated sperm oil.

2. The composition of claim 1 wherein the carboxylate salts are 0.25% manganese napthenate plus 0.25% chromium naphthenate.

3. The composition of claim 1 wherein the carboxylate salts are 0.50% manganese naphthenate plus 0.50% chromium naphthenate.

4. The composition of claim 1 wherein the carboxylate salts are 0.25% copper oleate plus 0.25% chromium naphthenate.

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